PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in or relating to the Production of Glycerol

We, E. I. Du Pont de Nemours and Co. of Wilmington, Delaware, United States of America, a corporation organised and existing under the laws of the State of Delaware, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to the production of glycerol from glycerol β-alkyl ethers of the general formula $CH_2OH.CHOX.CH_2OH$, where X is an alkyl group such as methyl, ethyl, propyl, butyl, isobutyl or a higher alkyl group. Such compounds may be made by the hydrogenation of the alkyl ethers of the alkyl glycerates as described in co-pending Application No. 3439/40 (Serial No. 541,360).

According to our invention glycerol is obtained by heating a glycerol β-alkyl ether in the presence of an aqueous solution of a hydrolysing catalyst, e.g. sulphuric acid, phosphoric acid, hydrochloric acid, hydrobromic acid or hydriodic acid.

The process may be carried out by refluxing a mixture of the glycerol β-alkyl ether and an aqueous solution of the hydrolysing catalyst at the ordinary pressure, or by heating the mixture in an autoclave at superatmospheric pressure. When working at atmospheric pressure with volatile halogen acid hydrolysing catalysts such as hydrochloric acid or hydrobromic acid, the molecular proportion of acid initially present is preferably at least equal to that of the ether so that the ether may react with the halogen acid to form glycerol and an alkyl halide, the latter being removed during the refluxing operation. When working under pressure, e.g. at pressures between 5 and 1000 atmospheres, quite small amounts of hydrolysing catalysts are sufficient, e.g. 0.5-5 per cent. by weight of the ether. In this case the ether is caused to react with the water to form glycerol and the alcohol corresponding to the alkyl group of the ether.

In the refluxing process the temperature of the mixture is generally between 90 and 115°C. In the autoclave process somewhat higher temperatures may be employed.

[Price 1/-]

The invention is illustrated by the following examples, in which the parts are by weight.

Example 1.

34 parts of glycerol β-methyl ether and 102 parts of aqueous hydrochloric acid containing 38% HCl were refluxed for four hours, methyl chloride distilling over during this period. The product was distilled to remove hydrochloric acid and water, and the residual mixture of glycerol β-methyl ether and glycerol was fractionated under reduced pressure. Glycerol was obtained in an 85.5 per cent. yield based on the glycerol β-methyl ether consumed.

Example 2.

41 parts of glycerol β-methyl ether and 141 parts of aqueous hydrochloric acid containing 20.7% HCl were refluxed for 3 hours at a temperature of 110-111°C., methyl chloride distilling over during this period. Aqueous hydrochloric acid was added throughout the run to maintain the concentration of acid substantially constant. The product was treated as in Example 1, and glycerol was obtained in a 97.5 per cent. yield.

Example 3.

48.5 parts glycerol β-methyl ether, 167 parts 20.7% aqueous HCl, 1.7 parts H.I and 0.6 parts $FeCl_3$ were refluxed for 3 hours, during which period methyl chloride distilled over. The product was treated as in Example 1 and glycerol was obtained in a 99 per cent. yield.

Example 4.

43.8 parts glycerol β-methyl ether, 151 parts 20.7% aqueous HCl and 3.0 parts tetraethylammonium chloride, $(C_2H_5)_4NCl$, were refluxed for 3 hours, during which period methyl chloride distilled over. The product was treated as in Example 1 and glycerol was obtained in a 98.8 per cent. yield.

Example 5.

51.0 parts glycerol β-methyl ether and 110.4 parts of aqueous hydrobromic acid (sp.gr. = 1.38) were refluxed for seven hours, during which period methyl bromide distilled over. The product was distilled and glycerol was obtained in a 44% yield.

Example 6.

61.4 parts glycerol β-methyl ether, 100

parts water and 6.1 parts aqueous hydriodic acid (sp.gr. 1.7) were heated for 4 hours in a silver-lined autoclave at 120-150°C. with a maximum pressure of 90 pounds per sq. in. The product was distilled and a 96.5 per cent. yield of glycerol recovered.

EXAMPLE 7.

77.8 parts glycerol β-methyl ether, 150 parts of water and 3.5 parts of 38% aqueous hydrochloric acid were heated for 3 hours in a silver-lined autoclave at 145-160°C. The maximum pressure was 110 pounds per square inch. The product was distilled and glycerol recovered in a 73.8 per cent. yield.

EXAMPLE 8.

52.2 parts glycerol β-methyl ether, 109.1 parts water and 4.6 parts 38% aqueous hydrochloric acid were heated for two hours in a silver-lined autoclave at 170-178°C. The maximum pressure was 142 pounds. The product was distilled and glycerol recovered in a 62.5 per cent. yield. Polyglycerol was likewise produced in a 27 per cent. yield.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process for the production of glycerol which comprises heating a glycerol β-alkyl ether in the presence of an aqueous solution of a hydrolysing catalyst.

2. A process according to Claim 1, in which the glycerol β-alkyl ether is glycerol β-methyl ether.

3. A process according to Claim 1 or 2, in which the glycerol β-alkyl ether is refluxed with the aqueous solution of the hydrolysing catalyst at the ordinary pressure.

4. A process according to Claim 1 or 2, in which the glycerol β-alkyl ether is heated with the aqueous solution of the hydrolysing catalyst in an autoclave at superatmospheric pressure.

5. A process according to Claim 1, 2, 3 or 4, in which the hydrolysing catalyst is an inorganic acid.

6. A process according to Claim 5, in which the hydrolysing catalyst is a halogen acid.

7. A process according to Claim 6, in which the molecular proportion of halogen acid initially present is at least equal to that of the glycerol β-alkyl ether.

8. A process for the production of glycerol, substantially as hereinbefore described with reference to each of the foregoing examples.

9. Glycerol, whenever obtained by the process of any of claims 1-8.

Dated the 22nd day of February, 1940.

E. C. G. CLARKE,
Solicitor for the Applicants.

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